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論 文 内 容 の 要 旨

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| 氏 名 (ZHU QIANG) | |
| 論文題名 | Study of charge state of Au nanoclusters on oxidized rutile TiO ₂ (110) surface by atomic force microscopy/Kelvin probe force microscopy (原子間力顕微鏡/ケルビンプローブフォース顕微鏡による酸化ルチルTiO ₂ (110)表面上へのAuナノクラスタの電荷状態に関する研究) |
| 論文内容の要旨 | |
| <p>Surface catalytic reactions based on metal oxide semiconductor have been widely researched for environmental treatment and energy conversion due to their unique properties of stability, and high activity. Rutile TiO₂ as one of the most typical catalysts has been proposed. In the TiO₂ catalytic system, Au nanoclusters are important for the catalytic reaction processes. To identify the charge states of Au nanoclusters and investigate the optimized charge state of Au for the oxidation of carbon monoxide (CO) at 78 K, I provided the following dissertation to summarize my doctoral research.</p> <p>In Chapter 1 of my research, I introduced the background of surface catalysis and the noble metal participated catalytic reactions. The aim was to highlight how Au can enhance the activity of catalytic reactions.</p> <p>In chapter 2, I introduced the theory of our experimental machine, which is based on scanning probe microscopy techniques.</p> <p>In chapter 3, I give the detailed description about the sample preparation of TiO₂(110) surface, and the setup of home-build ultra-high vacuum non-contact atomic force microscopy (NC-AFM).</p> <p>In chapter 4, I talked about the surface defects, such as oxygen vacancy, Ti interstitial, and polarons, which play a crucial role in adsorption properties of the surface reactants. Furthermore, the charge states of Au nanoclusters are influenced by surface and subsurface defects. One of the existing challenges in previous research is the confusion between the surface adsorption of water (H₂O), hydroxyl (OH), and the presence of surface defects such as oxygen vacancies (O_v). This confusion arises because the topographic images of OH and O_v exhibit similar contrast, making it difficult to distinguish between them. To resolve this problem, I combined the atomic force microscopy (AFM) with Kelvin probe force microscopy (KPFM) techniques to systematically identify the difference between H₂O, OH and O_v for the first time. Besides, the operation of H₂O and OH can be realized.</p> <p>In chapter 5, the adsorption and movement properties of CO molecules are investigated, which can be used to study the catalytic reaction of CO. CO molecules are not stable on the TiO₂(110) surface, how to move it to an appropriate reaction position is still a challenge. I found that oxygen adatoms (O_{ad}) play important role for CO adsorption at 78 K. And the unstable state CO can be stucked at the O_{ad} site. Moreover, I have achieved the movement operation of CO molecules in two-dimensional by oxygen modified tip apex. The result of CO movement in two-dimensions on TiO₂(110) surface will be of interest for the CO catalytic reaction at a precise site.</p> <p>In chapter 6, the charge states of Au nanoclusters are clearly identified, which is important to understand the positively charged or negatively charged Au participating the reaction processes of CO oxidation. By using KPFM measurement, I verified that surface and subsurface defects induced polarons and charge redistribution, which makes Au negatively charged. And the dipole moment from Au to the oxygen induces positively charged Au. I found that the negative charged Au nanoclusters are easily desorbed from the surface by operating technique, which indicates negatively charged Au does not stable for catalytic reactions at 78 K. Furthermore, I have successfully performed CO oxidation with oxygen, involving the participation of positively charged Au nanoparticles, for the first time at atomic resolution at 78 K. After reaction, positively charged Au obtain the electrons change into negatively charged.</p> <p>Chapter 7 is the conclusion and outlook for the future research of Au participated reactions based on surface catalysis.</p> | |

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

Surface catalytic reactions based on metal oxide semiconductor have been widely researched for environmental treatment and energy conversion due to their unique properties of stability, and high activity. In the TiO₂ catalytic system, the charge states of Au nanoclusters and investigate the optimized charge state of Au for the oxidation of carbon monoxide are important for the catalytic reaction processes. This dissertation summarizes the achievements of the research on (1) distinguishing between H₂O, OH, O_v and the manipulation of H₂O and OH on TiO₂(110) surface, (2) investigation of adsorption and migration properties of CO molecules and (3) identification of charge state of Au nanoclusters on oxidized rutile TiO₂(110) surface by atomic force microscopy (AFM)/Kelvin probe force microscopy (KPFM). The main achievements in the thesis are summarized as follows.

First, the surface defects of oxygen vacancy, Ti interstitial and polarons were studied, which play a crucial role in adsorption properties of the surface reactants. One of the existing challenges in previous research is the confusion between the surface adsorption of water (H₂O), hydroxyl (OH), and the presence of surface defects such as oxygen vacancies (O_v). This confusion arises because the topographic images of OH and O_v exhibit similar contrast, making it difficult to distinguish between them. To resolve this problem, the techniques of AFM and KPFM were used to systematically identify the difference between H₂O, OH and O_v for the first time. Besides, the operation of H₂O and OH can be realized.

Second, the adsorption and movement properties of CO molecule were investigated, which can be used to study the catalytic reaction of CO. CO molecules are not stable on the TiO₂(110) surface, how to move it to an appropriate reaction position is still a challenge. It was found that oxygen adatoms (O_{ad}) play important role for CO adsorption at 78K. And the unstable state CO can be stucked at the O_{ad} site. Moreover, the movement operation of CO molecules in two-dimensional was realized by oxygen modified tip apex. This result will be of interest for the CO catalytic reaction at a precise site.

Third, the charge states of Au nanoclusters influenced by surface and subsurface defects was investigated. By using KPFM measurement, surface and subsurface defects induced polarons and charge redistribution were verified, which makes Au negatively charged. It was found that the negative charged Au nanoclusters are easily desorbed from the surface by operating technique, which indicates negatively charged Au does not stable for catalytic reactions at 78K. It was also confirmed that the dipole moment from Au to the oxygen inducing positively charged Au. For the first time, CO oxidation with oxygen, involving the participation of positively charged Au nanoparticles has been successfully performed with atomic resolution at 78K.

As mentioned above, this thesis is a new study on the charge state of Au nanoclusters on rutile TiO₂(110) oxide surfaces by atomic force microscopy/Kelvin probe force microscopy. This thesis is not only a fundamental insight, but also an important issue for the application of catalysis and a significant contribution to the development of applied physics, surface science and especially nanocatalysis science. Therefore, this thesis is judged valuable as a doctoral thesis.